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Catalytic growth of carbon nanotubes and nanofibers on vermiculite to produce floatable hydrophobic "nanosponges" for oil spill remediation

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ABSTRACT

In this work, chemical vapour deposition (CVD) synthesis of carbon nanotubes (CNT) and nanofibers on the surface of expanded vermiculite (EV) was used to produce a highly hydrophobic floatable absorvent to remove oil spilled on water. XRD, SEM, TG and Raman spectroscopy showed that the carbon nanotubes and nanofibers grow on FeMo catalyst impregnated on the EV surface to form a "sponge structure". As a result of these carbonaceous nanosponges the absorption of different oils remarkably increased ca. 600% with a concomitant strong decrease of the undesirable water absorption.

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1. Introduction

Catalytic chemical vapour deposition (CVD) synthesis of carbon nanotubes (CNT) using a large variety of catalysts, e.g. Fe/Mo, Ni, Co, and different carbon sources, e.g. CH_4, C_2 and C_3 hydrocarbons, CO, ethanol, has been extensively investigated in the last years [1,2]. Due to its relative simplicity, low cost, high yields and the possibility to control several features of the CNT the CVD process has proven to be the most promising large scale carbon nanotubes preparation process. Different oxides such as Al_2O_3, SiO_2, MgO have been used as support to grow CNT [3–6]. Well defined surfaces, such as silicon wafer have also been used to grow highly organized aligned CNT known as "carpets" [7,8].

In this work, we have used the surface of vermiculite to grow CNT and nanofibers via CH_4–CVD synthesis. Vermiculite, a clay mineral, is a very interesting layered material with many potential industrial and environmental applications [9,10]. Upon sudden heating at temperatures higher than 700 °C inter lamellae water molecules evaporate abruptly, separating packets of layers that produce a highly developed porous structure. This expanded vermiculite (EV) shows a volume up to 20 times greater and floats on water due to the decrease in density, ca. 0.05–0.30 g cm^{-3} [9,11]. This vermiculite has been used to remove oil spilled on water due to the strong capillary action of the slit shaped pores [12–16]. A strong drawback of vermiculite is the high water uptake and low

absorption of the hydrophobic organic contaminants due to the strong hydrophilic clay surface. Several works and patents report different processes to hydrophobize the vermiculite surface using, for example, siloxanes [17] and polymer coating [13]. However, all these processes were relatively complex and produced relatively low oil removal capacity.

Hereon, we report the CH_4 CVD on the vermiculite surface to produce a dense CNT and nanofibers complex entangled structure. This nanostructured carbon produces a highly hydrophobic material with a "sponge" effect conferring to the absorbent a high oil removal capacity. This is one of the first environmental applications of carbon nanotubes.

2. Experimental

The vermiculite used in this work has the approximate composition $(Al_{0.30}Ti_{0.04}Fe_{0.63}Mg_{2.00})(Si_{3.21}Al_{0.79})O_{10}(OH)_2Mg_{0.13}$-$Na_{0.02}K_{0.10}(H_2O)_n$. The exfoliation was carried out by introducing the vermiculite in a quartz tube at 1000 °C for 60 s. The exfoliated vermiculite was impregnated with solutions of $Fe(NO_3)_3$ and $MoO_2(acac)_2$ using H_2O or methanol as solvents at different concentrations. The impregnated EV was dried at 80 °C for 3 h and submitted to the CVD process. The different prepared EV (ca. 1.0 g) was placed in a quartz tube of 40 mm diameter and heated at 10 °C min^{-1} to the reaction temperature of 900 °C under H_2/Ar flow (150 mL min^{-1}) and the temperature was kept at 900 °C for 1 h to pre-reduce the catalyst precursors. The material was then immediately submitted to a CVD with CH_4/Ar (1/1 mixture at 1 atm and 600 cm^3 min^{-1}) at 900 °C for 1 h. The reaction lasted for

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10 min, unless otherwise stated. After the reaction, the system was cooled under Ar flow.

The vermiculite–carbon composites were characterized by Raman spectroscopy (Renishaw) with the excitation wavelength of 633 nm and a laser spot size of 20 μm with confocal imaging microscope. The spectra taken at ten different points were averaged to minimize dispersion of the sample position.

The powder XRD data were obtained in a Rigaku model Geigerflex using Cu Kα radiation scanning from 2° to 75° at a scan rate of 4° min^{-1}. Scanning electron microscopy (SEM) analyses were carried out in a Jeol JKA 8900RL. TG analyses were carried out in a Hi-Res TGA 2950 thermogravimetric analyser (TA) instrument, with a constant heating rate of 10 °C min^{-1} under air flow (100 mL min^{-1}). BET surface area was carried out in an Autosorb 1 Quantachome using 22 cycles N_2 adsorption/desorption and the mercury porosimetry measurements were performed in a Quantachrome type PoreMaster 60 porosimeter.

The absorption experiments were carried simulating an oil spilling situation using 10 mL of contaminant, i.e. soy bean cooking, mineral oil and diesel, in 100 mL water. The produced hydrophobized vermiculite (100 mg) was then added to the suspension it of. After 5 min the vermiculite was removed using a simple metal sieve and left still for 3 min to drain the excess oil and water. Previous optimization experiments showed that the EV immediately saturates with both oil and water and contact times of 5 min are enough to reach equilibrium. Also, the drain time in the sieve has no significant influence on the amount of oil and water absorption. After absorption, the materials were weighed to determine the total amount of oil and water retained. For vegetable and engine oils the materials were dried at 80 °C overnight to remove water and weighed again to determine both the water and oil absorptions. For the experiments with diesel, the sample cannot be dried at 80 °C since a significant part of diesel will volatilize at this temperature. Therefore after absorption experiment the sample was weighed to determine the total amount of water and diesel absorbed. The sample was then extracted with 20 mL hexane and analyzed by gas chromatography (Shimadzu 17A equipped with FID capillary column Alltech EC-Wax 30m). From a simple calibration, the amount of diesel absorbed can be calculated from the total area of the peaks.

3. Results and discussion

3.1. Preparation and characterization of the composite EV/ nanostructured carbon

The composites vermiculite/carbon nanostructures were prepared by impregnation of $Fe(NO_3)_3$ and $Mo(acac)_2O_2$ in different concentrations on the vermiculite surface from methanol or water solutions. Table 1 shows the prepared precursors with different Fe-Mo/EV contents and the solvent used in the impregnation.

Table 1
Conditions used to prepare the different vermiculite precursors for the CVD synthesis.

Sample	Fe (wt%)	Mo (wt%)	Solvent
EV	–	–	–
Fe$_1$(W)	1	–	H$_2$O
Fe$_2$(W)	2	–	H$_2$O
Fe$_3$(W)	3	–	H$_2$O
Fe$_1$(M)	1	–	MeOH
Fe$_2$(M)	2	–	MeOH
Fe$_1$Mo$_{0.15}$(M)	1	0.15	MeOH
Fe$_2$Mo$_{0.30}$(M)	2	0.3	MeOH

The precursors were pre-reduced under H$_2$/Ar flow at 900 °C for 1 h and immediately submitted to a CVD with CH$_4$/Ar at 900 °C also for 1 h.

The obtained materials were characterized by SEM, TG, Raman spectroscopy and XRD. After CVD all samples were completely black due to carbon deposition. The samples prepared using water as solvent in the impregnation step were very brittle and fragile with almost total collapse of the lamellar vermiculite structure. As a result of this collapse the Fe(W) samples showed a small decrease on the surface area (Table 2). On the other hand, samples prepared with methanol showed the lamellar and porous structure intact and mechanically resistant.

Fig. 1a shows the scanning electron microscopy of the exfoliated vermiculite before CVD with regular flat surface lamellae and a slit-type porous structure. After CVD, the sample Fe$_1$(W) appears very brittle and no filaments or deposited material could be observed (Fig. 1b and c). On the other hand, SEM images for the Fe$_2$(M) and Fe$_2$Mo$_{0.30}$(M) (Fig. 2d–i) suggests that the EV completely changes the texture. A further magnification of the SEM image clearly showed a surface completely covered with carbon filaments with nanometric diameters and several micrometers long (Fig. 1e–i).

These materials with different forms of carbon were characterized by Raman spectroscopy. Spectra obtained with the laser 633 nm (Fig. 2) showed the presence of broad G bands at ca. 1595 cm^{-1} related to graphitic layers and the disorder D peak at 1330 cm^{-1}. The low I_G/I_D ratio of the samples Fe(w) without Mo (0.6–1.0) suggests the presence of high quantity of amorphous carbon or defects in the carbon structure. On the other hand, when Mo is introduced in the sample, i.e. Fe$_1$Mo$_{0.15}$(M) and Fe$_2$Mo$_{0.30}$(M), a very high I_G/I_D ratio of 3.2 and 7.9, respectively, was observed, suggesting the formation of well graphitized carbon. Also, it is interesting to observe that in the presence of Mo, the Raman spectra show strong bands at low wavenumber at 133–248 cm^{-1} related to the formation of single wall carbon nanotubes (SWCNT) with calculated diameters between 0.9 nm and 1.8 nm [18].

TG analyses for all Fe(M)/EV and FeMo(M)/EV samples after CVD showed a weight gain from 150 °C up to 550 °C (Fig. 3). This

Table 2
General properties of the EV composites prepared.

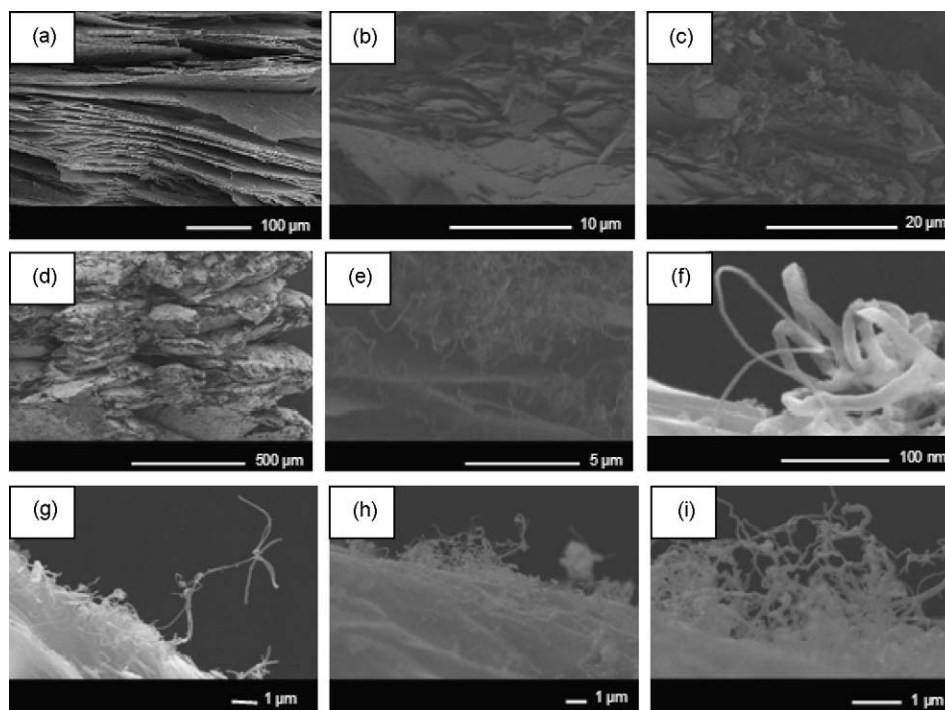| Sample	BET surface area (m^2 g^{-1})	Hg porosimetry (cm^3 g^{-1})	C^a (%)	Forms of carbon^b	Average oil absorption (g g^{-1})	Water absorption (g g^{-1})
EV	5	1.9	–	More amorphous	0.5	3.7
Fe$_1$(W)	3	–	Ca. 0.1	More amorphous	–	–
Fe$_2$(W)	3	–	Ca.0.1	More amorphous	–	–
Fe$_3$(W)	2	1.6	Ca.0.1	More amorphous	–	–
Fe$_1$(M)	7	–	Ca.0.7	More amorphous	1.7	0.5
Fe$_2$(M)	9	1.8	ca.2	More amorphous	1.3	0.5
Fe$_1$Mo$_{0.15}$(M)	15	1.8	ca.2	SWCNT and graphitic carbon	3.2	0.5
Fe$_2$Mo$_{0.30}$(M)	18	1.7	ca.2	SWCNT and graphitic carbon	2.0	0.5

^{a} From TG.
^{b} Obtained from the I_G/I_D ratio and from SEM analyses.

Fig. 1. SEM images of EV before hydrophobization (a) and after CVD with CH_4 at 900 °C for 1 h for $Fe_1(W)$ (b and c), $Fe_2Mo_{0.30}(M)$ (d–g) and $Fe_2(M)$ (h and i).

increase is related to the oxidation of iron, molybdenium and other metals in the EV which were reduced by H_2 during the CVD process. Weight losses observed at higher temperatures should be related to carbon oxidation and were used to estimate the amount of carbon deposited. TG of samples prepared by Fe impregnation with water, showed in general a weight loss of only ca. 0.1–0.2%, suggesting that no significant amount of carbon material was formed. This result suggests that water is not a good solvent for Fe impregnation on EV. Simple soaking in water strongly decreases the EV mechanical resistance. Moreover, as vermiculite is a cation exchange material, the Fe^{3+} from solution can migrate into the EV lamellar structure. Upon pre-reduction with H_2, the interlayer Fe^{3+} is converted to Fe^0 which might lead to a collapse of the local clay structure. Also, during impregnation, Fe^{3+} in H_2O can hydrolyze to

produce insoluble large particles of $Fe(OH)_3$ which should be less active to produce carbon during CH_4 CVD.

On the other hand, the samples prepared with methanol $Fe_1(M)$ and $Fe_2(M)$ showed weight losses of ca. 0.7% and 2%, respectively, suggesting that the Fe content directly affects the amount of carbon deposited. The relatively high oxidation temperature, i.e. 520 °C, indicates the presence of a well organized carbon. In the catalysts FeMo(M), ca. 2% carbon was formed with a lower oxidation temperature (440 °C), suggesting that Mo has an important effect on the types of carbon deposited.

It was observed by XRD (Fig. 4) that the CVD process does not affect the EV crystalline. It can be observed a small peak at 46° after the reduction step suggesting the presence Fe metal. It was not possible to observe any reflection peaks related to Mo.
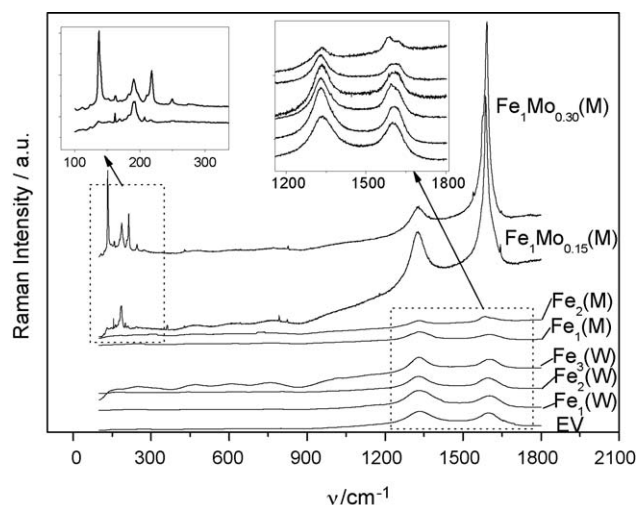

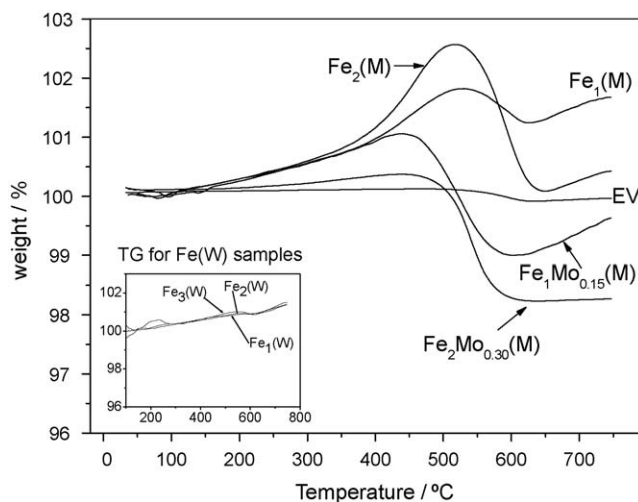**Fig. 2.** Raman spectra of the composite EV/nanostructured carbon material.

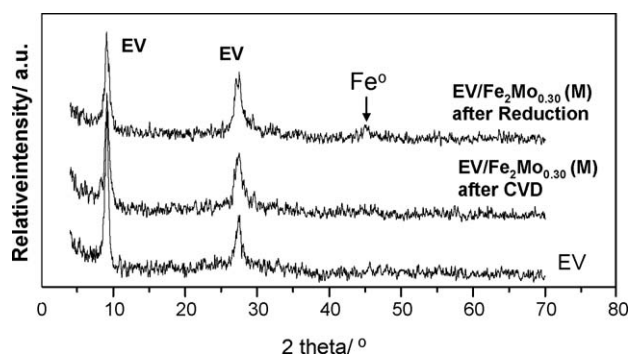**Fig. 3.** TG of the composite EV/nanostructured carbon material, in air.

Fig. 4. XRD for the pure EV, EV/Fe$_2$Mo$_{0.30}$(M) after reduction and EV/Fe$_2$Mo$_{0.30}$(M) after CVD process.
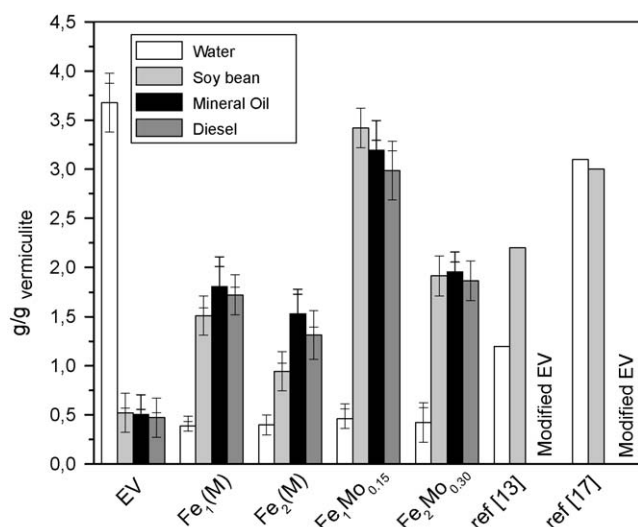

Fig. 5. Absorption of water and spilled oils (soy bean cooking, mineral oil and diesel) by the hydrophobic vermiculite–nanostructured carbon composites and two other modified EV absorbents described in the literature [13] and commercially available [17].

3.2. Oil removal studies

For the oil removal studies three different model contaminants were used, i.e. vegetable oil (soy bean), mineral oil and diesel. The obtained absorption capacities for water and for the different oils are shown in Fig. 5

It can be observed that the EV before CVD absorbs a high amount of water ca. 3.5 g g^{-1} but low absorption capacities for the oil contaminants, ca. 0.5 g g^{-1}. For the composites Fe$_1$(M) and Fe$_2$(M) better results were obtained with the decrease of the H$_2$O absorption to 0.5 g g^{-1} and a general increase on the oil removal capacity 1.3–1.7 g g^{-1}. On the other hand, for the composite Fe$_1$Mo$_{0.15}$(M) a remarkable improvement is observed with H$_2$O absorption strongly decreasing to 0.5 g g^{-1} with oil removing capacities of 3.5 g g^{-1}, 3.7 g g^{-1} and 3.8 g g^{-1} for vegetable, engine and diesel, respectively.

In order to rationalize the changes observed on the absorption properties, Table 2 compares several parameters, such as the BET surface area, Hg porosimetry results, carbon content and its forms for the different composites.

BET surface areas do not vary significantly after CVD for the samples Fe(W) and only a small increase is observed for the Fe(M). On the other hand, an important increase on the surface area is observed for the samples FeMo(M) reaching 18 m^2 g^{-1}. This

increase is likely related to the large area on the walls of nanotubes and nanofilaments grown on the EV surface. As the amount of carbon deposits is small, ca. 2 wt%, no significant change was observed in the macropore volume, as suggested by Hg porosimetry. When these results are analyzed three main factors seem important for the absorption properties of EV, i.e. the hydrophobicity of the surface, the nanotubes/nanofibers sponge structure and the pore volume available for absorption. All composites were covered with a layer composed of different forms of carbon, e.g. amorphous, graphitic, fibers, and tubes. All these carbon forms are very hydrophobic in nature and should produce a very water repellent environment. For this reason the water absorption by EV decreases from 3.5 g g^{-1} to ca. 0.5 g g^{-1} after CVD. Also, this hydrophobic character leads to a better interaction with the hydrophobic oil molecules and should lead to a general increase in oil absorption. Nevertheless, the composites FeMo(M) showed an unexpectedly high oil absorption. Although the reasons for this behavior are not clear they can be related to the carbon nanostructures present in these composites. The nanotubes and nanofibers on the EV lamellae should offer extra surface for the interaction with the oil contaminants as observed by BET. Also, these entangled tubes and fibers produce a sponge-like structure which should have a strong capillary effect favoring the up take of the more viscous oils. In general, oils have much higher viscosity, e.g. 70–80 cP for vegetable, diesel and crude oils, compared to water (1 cP) and the penetration of EV pore structure should be a critical step.

As expanded vermiculite absorbs liquids into the inter-lamellar space, the third important factor affecting the oil absorption is the pore space available. It can be considered that the carbon structures produced in the inter-lamellae space do not cause a significant change in pore volume as suggested by Hg porosimetry. For this reason the maximum amount of liquid absorbed (water + oil) is nearly the same for EV and FeMo(M), considering that water and oil have similar densities, 1 and 0.9–0.95 g cm^{-3}, respectively. Moreover, materials with higher BET surface area, e.g. FeMo(M) do not show increased liquid (oil + water) removal. This reinforces the idea that the pore volume filling by absorption rather than adsorption is more important to define the amount of retained liquid.

Fig. 5 also shows the oil and water absorption for two other modified EV absorbents described in the literature [13] and commercially available [17]. Although different EV were used to produce these materials which should have some effect on the oil removal capacity, it can be observed that the composite Fe$_1$Mo$_{0.15}$ is much more efficient with higher oil removal capacity and low water retention. This much lower water absorption reflects the strong hydrophobic character of the carbon deposits compared to the other hydrophobization processes used in refs. [13] and [17].

We have also carried an experiment with engine oil spilled in water with 3.5% dissolved NaCl to simulate sea water. The obtained results showed no significant effect of NaCl on the absorption properties of Fe$_1$Mo$_{0.15}$(M).

4. Conclusion

CH$_4$-CVD can be used to grow carbon nanotubes and nanofibers on the surface of EV with FeMo impregnated catalysts. The produced carbon/EV nanostructured composites showed high efficiency to absorb different oils (soy bean, engine, diesel) with a remarkable decrease on H$_2$O absorption. These results were discussed in terms of: (i) a strong hydrophobic character produced by the carbon structures, (ii) an increase on surface area which favours interaction with the oils and (iii) a "sponge" effect produced by the entangled nanofibers and nanotubes favoring capillarity. Moreover, the CVD process does not cause any

significant change in the EV pore volume available for liquid absorption. This novel floatable absorbent/adsorbent can be produced by a simple process using low cost and available chemicals and showed very promising results to be used in environmental remediation especially in oil spilled on waters.

Acknowledgements

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